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Improved Round Trip Efficiency for Air Independent Regenerative Fuel Cell Systems

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Executive Summary

The goal of this Office of Naval Research sponsored project is to develop high energy density energy storage systems for unmanned underwater vehicles (UUVs). ONR is interested in regenerative fuel cells (RFCs) for UUV applications due to the capability for high energy storage density vs. batteries. Improved fuel cell and electrolyzer efficiencies are desired for higher energy density and faster refueling times. ONR funded the first phase of this effort as a collaborative project between Proton Energy Systems (d/b/a Proton OnSite) and W.L. Gore to make advancements in membrane technology, increasing the electrolyzer efficiency. The focus was on incorporation of reinforced membranes to enable lower ionic resistance through membrane thickness reduction. This first phase was previously reported. The second phase included building upon past work on air independent RFC systems to extend the capability of an RFC breadboard system and develop key components to enable long duration undersea missions.

In developing technology for air independent undersea vehicle missions, a ground-test breadboard system was adapted and utilized to prove advanced components that enable closed-loop, zero emission, low signature energy storage. The system utilizes proton exchange membrane (PEM) fuel cell and electrolysis technology with proven commercial reliability, and a balance-of-plant primarily consisting of commercial-off-the-shelf (COTS) components. Objectives included refurbishment of the system to improve operability, including upgrading the power capability of the system to take full advantage of the rated stack power. The results of cycle testing at increased output power included demonstration of 34 consecutive cycles. Initial durability testing measured the magnitude of reactant loss to the ambient atmosphere, before replacing components known to contribute to this loss as observed during tests in a previous program. Advanced components to mitigate these losses were designed and tested at a bench-top level before integrated testing within the breadboard system. A final round of cyclic testing was conducted with advanced reactant circulation during fuel cell power generation as well as complete hydrogen recovery during the electrolysis recharge period. A model of a refined system package and the demonstrated electrochemical performance predict that 400 Wh/L is achievable in the near-term.

1.0 Introduction

In developing technology for air independent undersea vehicle missions, a ground-test breadboard system originally supporting stratospheric air vehicle technology has been adapted and utilized to prove advanced components that enable closed-loop, zero emission, low signature energy storage. The system utilizes proton exchange membrane (PEM) fuel cell and electrolysis technology with proven commercial reliability, and a balance-of-plant primarily consisting of commercial-off-the-shelf (COTS) components. Custom components were designed to replace the components that allowed reactant loss to ambient during early tests. The gross output power level increased from two to greater than four kilowatts. Initial durability testing measured the magnitude of reactant loss. The results of cycle testing at increased output power include demonstrating 34 consecutive cycles. Bench-top testing of advanced components led to integrated testing within the breadboard system. A model of a refined system package and the demonstrated electrochemical performance predict that 400 Wh/L is achievable in the near-term.

1.1 Project Objectives

The purpose of this phase of the effort is to advance the understanding, implementation, and operational testing of the features that enable a regenerative fuel cell (RFC) to simultaneously be truly air independent and have high energy density.

Objectives:

- Upgrade RFC system to enable full 4.4 kW fuel cell power output (previous system operated at 2 kW)
- Demonstrate improved closed loop capability through reduction of known mass losses: development of hydrogen recovery reactor and hermetically sealed compressors
- Perform durability testing on the existing RFC breadboard and refine startup and shutdown control systems

1.2 Background

Navy underwater vehicle platforms (UUV, ASDS, SWCS, etc.) are demanding larger and larger energy storage capacities to accommodate longer underwater missions and increased platform power requirements. New energy storage devices with high volumetric energy density for underwater vehicles, both manned and unmanned, are therefore needed, such as regenerative fuel cell (RFC) systems based on proton exchange membrane (PEM) technology. An RFC consists of a fuel cell powerplant, an electrolysis system for recharging the reactants, and reactant storage. These water-based energy storage systems have been shown to perform substantially better than traditional battery systems in areas such as rechargeability, specific energy density, and reliability. Advanced membrane and catalyst materials will enable higher efficiency electrolysis, substantially improving the practical energy density for regenerative fuel cell applications.

Initial study focused on membrane development and was reported on previously. The next step addressed operation of Proton's regenerative fuel cell system at the full 4.4 kW fuel cell design point and in a truly closed loop mode (proposal tasks 2, 3, and 4). The research objectives for Phase 2 were broken into the following separate subtasks: (1) Air Independent RFC Component

Durability Testing, (2) Dissolved Hydrogen Recovery Reactor, and (3) Hermetically Sealed Reactant Circulation Compressors.

2.0 Technical Approach

A regenerative fuel cell (RFC) is an energy storage device that combines a fuel cell system, a water electrolysis system, and reactant storage. A hydrogen-oxygen RFC stores and utilizes both of the key products from the electrolyzer, hydrogen and oxygen, as opposed to an air-breathing system that would store the hydrogen and rely on the presence of oxygen in the ambient environment. A closed-loop hydrogen-oxygen RFC conserves mass in the cycle of: a) producing hydrogen and oxygen from water in the electrolysis process, and b) producing and recovering water in the fuel cell process. A closed-loop hydrogen-oxygen RFC enables high specific energy storage (400-1000 Wh/kg) for environments with very low to zero ambient oxygen such as the stratosphere, under water, earth orbit, and other space exploration applications [1-2].

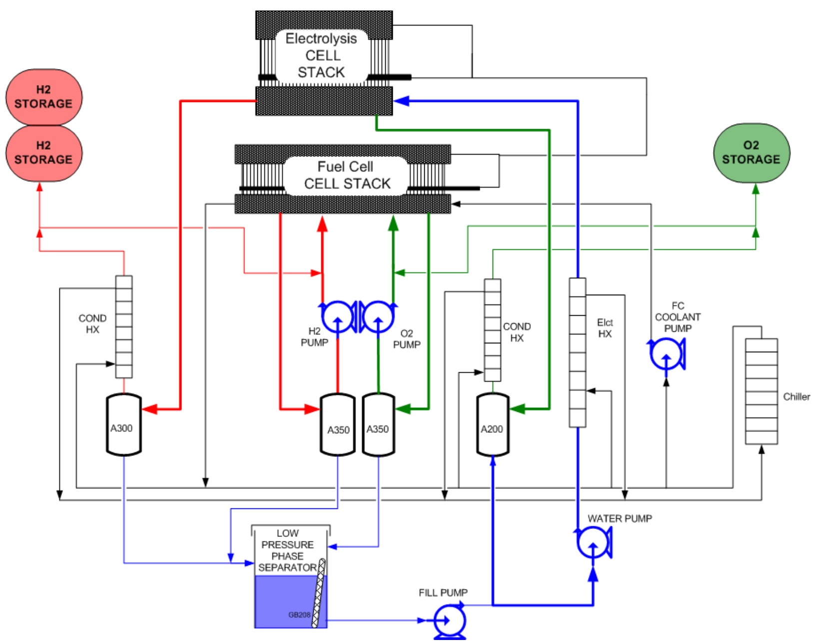

Figure 1. Simplified system diagram for the tested RFC breadboard

With the testing conducted for the stratospheric air vehicle mission as background, the two known mass losses from the previous configuration were addressed. The first is in effect during the recharge operation where dissolved hydrogen from the hydrogen water phase separator leaves with periodic water draining. The water is recaptured in a low pressure water tank, but the dissolved gas is allowed to come out of solution and escape to the ambient environment. The dissolved hydrogen recovery reactor (Task 3) was devised to address this loss. The second loss is in effect during the fuel cell power cycle from the hydrogen and oxygen circulation compressors. The base components used for this function did not maintain a tight overboard seal. This loss is addressed through Task 4 where hermetically-sealed versions of the same style compressor are developed. In parallel with these component developments, Task 2 incorporated advancing the capabilities of the breadboard to demonstrate higher power output and enhanced control algorithms, and culminated with verification testing using the components developed in the other tasks.

The experiments described below address verifying the leak rate of the baseline system, screening reactor media for dissolved hydrogen recovery effectiveness, and verifying a reduced leak rate after installing the hydrogen recovery reactor and the sealed reactant circulation compressors into the breadboard system.

2.1 Dissolved Hydrogen Recovery Reactor (Task 3)

While operating at 400 psig in anticipation of the stratospheric air vehicle, the concentration of dissolved hydrogen would be small, but the total mass loss would become significant over a year or more of continuous operation without maintenance. The undersea application does not require the same duration of unattended operation. However, undersea missions do require higher volumetric energy density, leading to an electrolysis operating pressure in the range of 2,400-5,000 psig. As a result of the higher pressure and higher concentration of dissolved hydrogen, hydrogen recovery becomes important even for shorter durations. A solution for recovering dissolved hydrogen is to drain the water stream through a catalyzed bed in the presence of water circulating with dissolved oxygen. Since the electrolysis anode water circulation loop is operating slightly below the hydrogen pressure, a small amount of dissolved hydrogen will come out of solution and be catalytically combined with available oxygen to form water.

The effectiveness of the reactor media at scavenging was characterized in two ways: (1) impact on electrolysis water quality, and (2) reduction in hydrogen concentration in the oxygen head space in the electrolysis anode loop. The impact on water quality was measured by starting with a known deionized water resistivity and then introducing circulation through the reactor media. The change in water resistivity was monitored over a period of 10-15 minutes. The bench-top hydrogen scavenging test utilized a sub-scale electrolysis system to feed pressurized hydrogen rich water into a sub-scale reactor circulating oxygen rich water at ambient pressure. The hydrogen pressure was about 200 psi above the oxygen pressure, representing a worst-case for bubbles coming out of solution. The atmosphere within a separate water tank in the oxygen circulation loop was monitored with a combustible gas detector. Four types of reactor media were evaluated using three different processing techniques.

Finally, a reactor vessel was designed for the full-scale breadboard system. It was designed to operate at 2,400 psig to make it applicable to future high pressure versions of the RFC system. Once installed in the full-scale breadboard, the hydrogen phase separator drain was directed to the reactor vessel once the electrolyzer was in steady state operation. The oxygen atmosphere was monitored with periodic manual purges through a combustible gas sensor. This initial manual experimentation can be utilized to develop an algorithm for automation of the test to gather more data.

2.2 Hermetically-Sealed Reactant Circulation Compressors (Task 4)

The reactant circulation compressor work was primarily conducted by a sub-contractor. Once the sub-contractor completed its design and fabrication work, they initiated the testing of the new hardware. They utilized air as the working fluid to measure the oxygen compressor flow and pressure drop. In addition to also using air for testing the hydrogen compressor, they utilized helium on a limited basis to test the hydrogen compressor.

Upon receipt at Proton, the compressors were run on the bench-top to verify basic functionality and they were leak checked with a nitrogen pressure decay test.

2.3 Air Independent RFC Component Durability Testing (Task 2)

The breadboard leak rate measurements were conducted by operating through a charge-discharge cycle. The cycle starts with a ramp of current input to the electrolysis stack (1) followed by a period of charging the gas storage via electrolysis (2). When the storage tanks are full, the electrolysis system transitions to its stand-by condition (3) simultaneously with the fuel cell stack ramp to full power output (4). The electrolysis system maintains a steady-state stand-by condition (5) while the fuel cell operates as the primary power supply (6). When the discharge cycle reaches a certain time or a minimum reactant storage pressure, the fuel cell transitions to its stand-by condition (7). The cycle repeats when the electrolyzer begins its start-up ramp (1). The leak rate was measured in two ways. First, the slope of the oxygen pressure at equivalent points in the charge-discharge cycle was plotted. Second, the water level in the water supply tank was tracked with a continuous level sensor.

The RFC component durability testing was conducted over several rounds. In the first round of testing, the breadboard was refurbished to an operational state and an initial upgrade of the fuel cell reactant pressure regulation was undertaken. This work allowed operation at 2.2 kW to obtain a set of baseline leak measurements. In the second round of testing, the fuel cell coolant circuit was upgraded and the fuel cell reactant pressure regulation was further upgraded on the oxygen side. These upgrades allowed operation of the system at greater than 4 kW gross output from the fuel cell. Finally, the sealed scroll compressors from Task 4 and the full-scale dissolved hydrogen recovery reactor from Task 3 were incorporated into the breadboard to test their effectiveness at reducing leaks and achieving a fully closed-loop system.

3.0 Results and Discussion

Based upon the technical approach described above, a detailed plan was developed and executed for the refurbishment of the breadboard test system. A complete design and fabrication effort was completed for the hydrogen recovery reactor and the hermetically-sealed reactant circulation compressors. The milestone table is shown below.

Table 1. Milestone Summary

Task Number	Project Milestones	Task Status	Progress Notes
2	Complete test stand refurbishment	100%	Complete
2	Complete baseline testing of recommissioned unit	100%	Complete
3	Complete hydrogen recovery reactor testing	100%	Tested at full scale
4	Procure hermetically sealed compressors	100%	Received, installed, tested
2	Complete upgrade fabrication/installation	100%	Complete
2	Initial multi-day full power testing	100%	Complete
1	Project Management	100%	Complete

Breadboard testing was executed in three rounds. In the first round, some components were refurbished or upgraded and operational testing in electrolysis and fuel cell modes was conducted. Baseline leak rates were measured. In the second round, additional upgrades in the fuel cell coolant circuit and fuel cell reactant pressure regulation were implemented and the gross power output of the system was increased to greater than 4 kilowatts, twice the previous power output. In parallel with the first two rounds of breadboard testing, materials development for the hydrogen recovery reactor media took place through sub-scale bench-top screening tests.

In the final round of breadboard testing, the full-scale hydrogen recovery reactor and the hermetically-sealed scroll compressors were installed. Full-scale system cycle testing verified the functionality of the scroll compressors to meet the fuel cell reactant circulation requirements without leaking at a meaningful, measurable rate. In addition, the hydrogen recovery reactor proved to be effective at merging the drain effluent of the electrolysis hydrogen phase separator with the electrolysis anode water circulation loop.

The design and test program accomplished all of its major goals and successfully demonstrated the feasibility of a 4 kilowatt, air independent, regenerative fuel cell. The results of the project are further described broken down by project task below.

3.1 Dissolved Hydrogen Recovery Reactor

The dissolved hydrogen recovery reactor is a passive catalyzed reactor that allows the pressurized water containing dissolved hydrogen in the electrolysis phase separator to be drained and mixed with the electrolysis anode water. The baseline breadboard system allowed that water to drain to a low pressure water vessel, which allowed the dissolved hydrogen to escape (Figure 2). This loss does not have a significant efficiency impact at 400 psig, but the higher the pressure, the larger the impact (Figure 3). As the intention for this type of system is to realize the volumetric energy density gains at 2,400 or 5,000 psig, it was important to begin the design of this reactor vessel and its media.

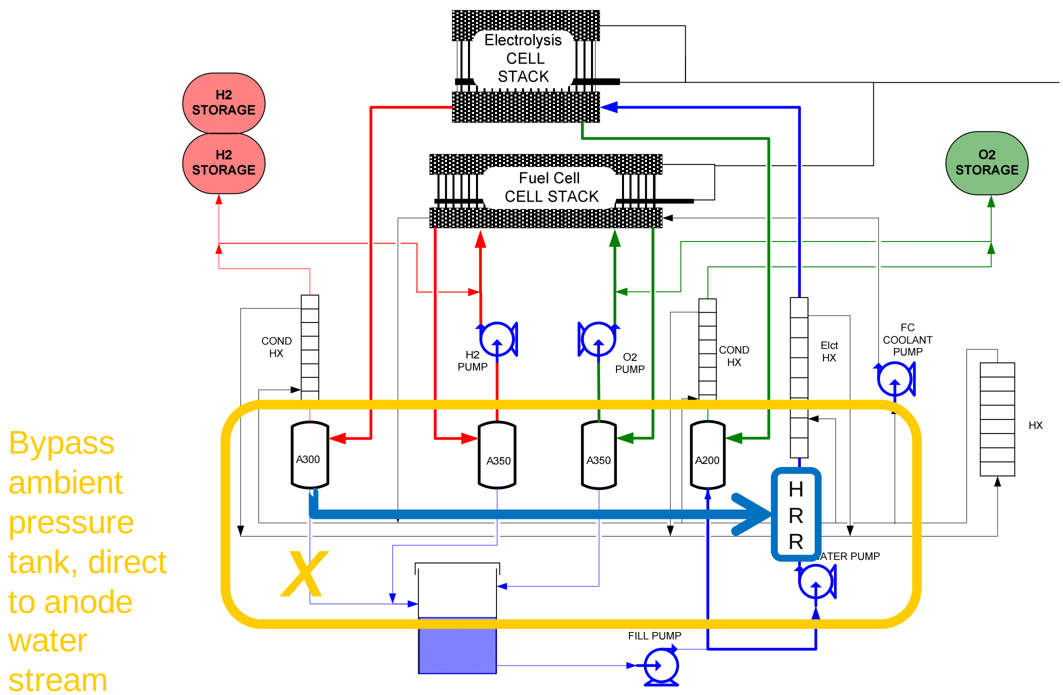

Figure 2. A schematic that depicts the change in drain flow when employing a dissolved hydrogen recovery reactor vessel

Hydrogen concentration in water									
		(N-cm3/g)			(ppm)			Hydrogen loss rate	
Pressure	Pressure	Temperature (deg. C)			Temperature (deg. C)			(25 C)	(50 C)
(Mpa)	(psig)	0	25	50	0	25	50	% gross	% gross
3	420	*0.643*	***0.566***	*0.489*	*15.31*	***12.35***	*9.84*	*0.4%*	0.3%
16.7	2407	*3.517*	***3.102***	*2.686*	*466.0*	***376.5***	*300.8*	*2.2%*	1.9%
35	5062	*7.114*	***6.292***	*5.470*	*1975*	***1600***	*1284*	***4.4%***	**3.9%**

Figure 3. Hydrogen loss rate calculations as an efficiency impact at 400, 2400 and 5000 psig

The dissolved hydrogen recovery reactor task began by designing the required vessel for full-scale operation and developing bench-top test hardware to conduct sub-scale testing. Even though the current breadboard is only rated for electrolysis operation up to 400 psig, the reactor vessel was designed for operation at 2,400 psig to make the design applicable to the next iteration of the system design. Calculations were performed to verify the structural integrity of the vessel, the threads, and the O-ring seals with sufficient safety factor. Furthermore, a system was designed to capture the reactor media and keep it contained under high water flow. The results of the reactor design and fabrication efforts are shown in Figure 4, as well as installed in the system (Figure 7).

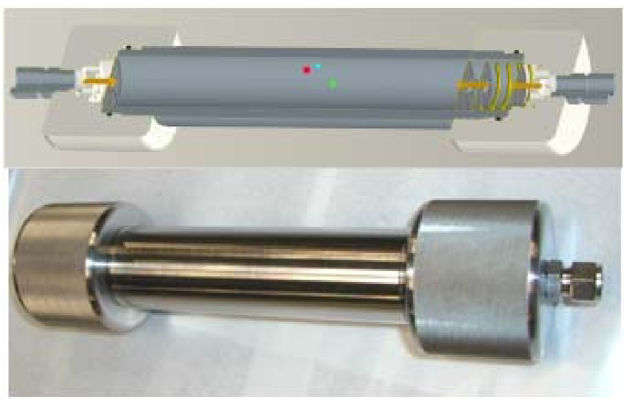

Figure 4. Reactor vessel design (top) and fabricated prototype (bottom)

The design concept for the reactor media was to utilize ion exchange resin media from water treatment polishing beds as the base. The catalytic material would be introduced by applying Proton's proprietary procedures developed for other applications. Ion exchange resins were sourced in loose bead form factor from 3 suppliers and were processed both as anion/cation mixtures as well as single species. The evaluations were designed to assess: (1) how well the resin held up to the treatment process, (2) if the resin continued to function as originally intended for water treatment, and (3) if the resin successfully took on the added functionality of catalyst substrate for hydrogen recovery. Initial visual screening using optical and electron microscopy revealed that some of the resin bead shapes were broken at the microscopic level, but the microscopy samples were not large enough to assess if this phenomenon was widespread, if it was due to Proton's processing, or if the variety of shapes and cracks was present in the untreated material at the same fraction.

The reactor media screening began by measuring the effect of the media on a circulated bath of deionized water. A decrease in water quality would have indicated that the processing done to the media may have initiated a chemical breakdown of the base material. All combinations of base media and various processing trials showed a relatively stable result with minimal negative impact on water quality. Interestingly, the only samples that exhibited a negative trend on water quality were those that had not been treated with the catalyst processing. Media A showed the most stability in performance before and after treatment. However, both B and C exhibited a stable trend with time after treatment. Therefore, all three were evaluated in the dissolved hydrogen test. Examples of the single species results are shown in Figure 5.

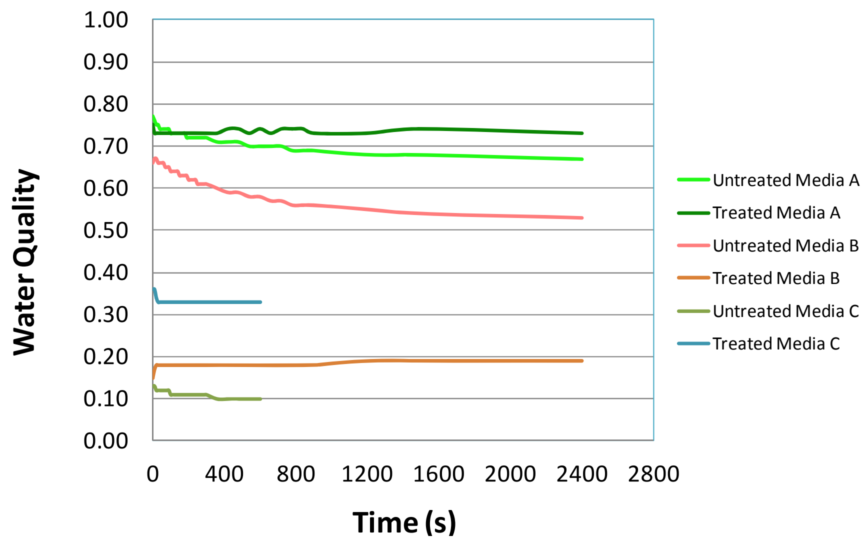

Figure 5. Reactor media screening by measuring effect on deionized water quality over time

Following the water quality screening, the reactor media samples were tested for their impact on scavenging dissolved hydrogen. A PEM electrolysis cell generated a 200 psig stream of hydrogen and water and an ambient pressure stream of oxygen and water. The volume flow rate of circulated anode water was approximately a factor of 70-100 times greater than the flow rate of hydrogen rich water injected into the reactor.

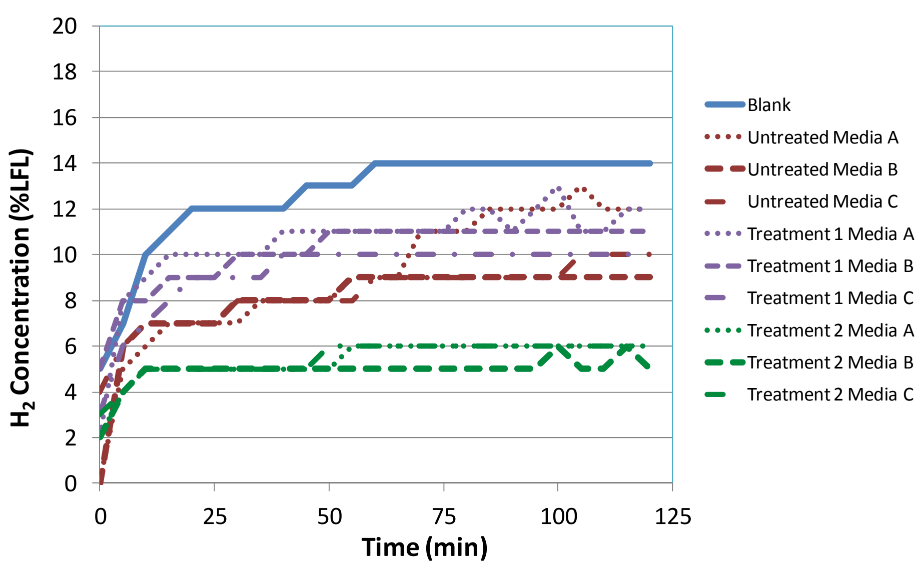

Figure 6. Reactor media screening by measuring effectiveness at scavenging dissolved hydrogen

The level of hydrogen concentration in the oxygen atmosphere was measured in an ambient pressure tank downstream of the reactor vessel. An initial grouping of samples ("Treatment 1") reduced the concentration by a factor of 1.1-1.5 compared with the blank. However, they were similar in performance to the untreated reactor media indicating that the treatment process was not adding value. By increasing the duration of the treatment process ("Treatment 2"), the final processing trial achieved a clear difference in the performance, reducing the concentration by a factor of three compared with the blank and a factor of two better than the untreated media. Examples of the plots of hydrogen concentration over time are shown in Figure 6. As all three media types performed well with Treatment 2, Media A was selected for the full-size bed based on the higher stability it exhibited during the water quality screening.

Finally, the configuration of the media within the finished bed was selected. In order to gain the functionality of hydrogen recovery along with water polishing, each reactor bed had stratified layers of the selected treated media (Treatment 2, Media A) and untreated media. The configuration selection was an engineering estimate, and further configuration studies could be conducted in the future if they prove necessary.

Figure 7. Full-scale hydrogen recovery reactor vessels installed in the breadboard system

3.2 Hermetically-Sealed Reactant Circulation Compressors

The scroll compressors installed in the initial version of the breadboard proved to be effective for fuel cell reactant circulation. They achieve high flow rates with relatively low head pressure. However, the COTS version of the scroll compressor does not seal with high integrity from leaking to the ambient environment. For the long-term effectiveness of the scroll compressor in an air independent system, it is desirable in all cases and necessary in most cases for the reactant mass within the system to be conserved. While the pressure and flow characteristics of a scroll compressor are desirable, it needed to be made with overboard seal integrity. As a result, the manufacturer of the COTS components was engaged to develop a more advanced version of the scroll compressor. The design effort proceeded with a staged conceptual and final design with Proton reviewing and approving the design output at each stage.

To achieve longest durability of the total RFC system, the scroll compressor materials were chosen to be compatible with electrolysis cell stack water. This included selecting a stainless steel housing, stainless steel encapsulated magnetic couplings and ceramic bearings. In addition, to keep the overall system as compact as possible, the design utilized a single DC motor to actuate two compressor heads, one for hydrogen circulation and one for oxygen circulation. The flow rates for the two compressor heads could be adjusted by adjusting the flow area within the heads while still operating at the same rotational speed.

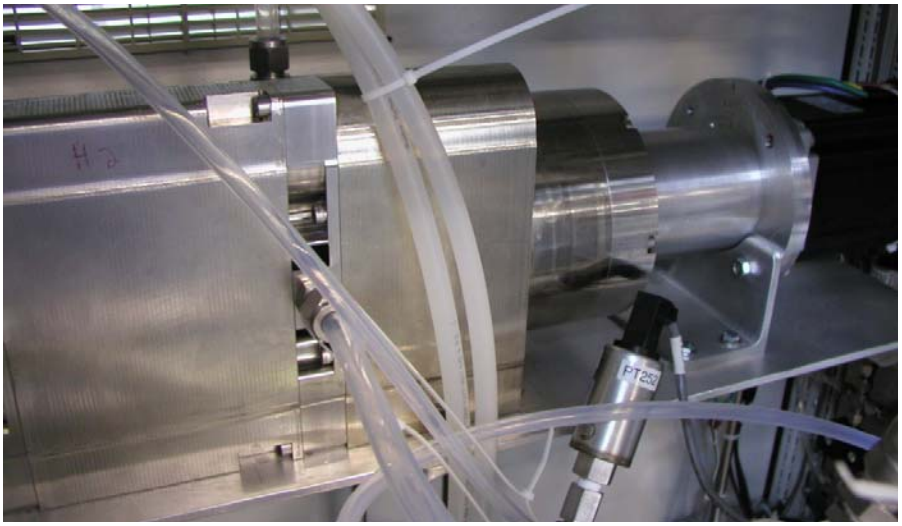

Figure 8. Finished scroll compressor as installed and tested in the breadboard system

The stainless steel encapsulated magnetic couplers proved to be challenging to procure and they became a very long lead item. The biggest challenge, however, turned out to be the ceramic bearings. An initial review of the material properties indicated they would have the strength and stiffness required for functionality. However, once they were installed in the final article, they proved to deflect too far to maintain the tight clearances between the fixed and moving scroll heads. As a result, we reverted to a more conventional bearing to permit the final round of testing. This conventional bearing might prove to have some long-term contamination effects for the electrolysis cell, but the pathway to cause contamination is tortuous and it was not deemed to be a problem for this short duration test. Additional study on the ceramic bearings is needed to avoid this risk and maintain consistency with the original design intent, but for the purposes of showing feasibility of the hermetically sealed compressors to reduce reactant loss, the existing bearings were sufficient.

After several schedule delays, the new sealed hydrogen and oxygen reactant circulation components were received from the supplier. There was some minor damage in shipping that was repaired at Proton. After repairing the damage, bench-top tests for flow were conducted to verify operation. Furthermore, a pressure decay test was conducted to verify that the compressor unit does seal overboard. The quality of construction was high, and the combined circulation unit met the initial requirements for flow and sealing. After the bench-top tests, the compressor unit was installed in the breadboard system for the final round of breadboard testing (reported above).

3.3 Air Independent RFC Component Durability Testing

The breadboard level component durability testing was undertaken in three rounds. Preceding the first round of testing, the system was evaluated and the results from previous testing were reviewed. From that review, several minor items were identified as requiring refurbishment before re-starting the system. These components included the fuel cell pressure regulators and phase separators and the electrolysis water filter. These items had limited overall performance and test expediency during the original MDA test program. Furthermore, it was identified that it would be advantageous to implement some of the anticipated plumbing modifications associated with the hydrogen recovery reactor (HRR) during the initial modification phase. Because the HRR installation impacts the pressurized oxygen loop within the electrolysis system, oxygen cleaning and pressurized oxygen assembly techniques were necessary. Completing the HRR hard-pipe modifications up-front allowed the system to be moved into the clean-room assembly area once rather than requiring multiple iterations. Since the scroll compressor plumbing modifications would all be within the low pressure fuel cell recirculation loop, clean-room logistics were not a concern for that work.

After completing the initial upgrades, the first round of testing started. This round of testing first involved some initial operation with “manual” operation via graphical user interface button control. Manual operation was conducted in both fuel cell and electrolysis modes of operation. As the system software tuning progressed, the system was cycled between charge and discharge modes to establish a baseline set of leak rate measurements.

System level mass losses were measured using the full RFC breadboard (Figure 5). Measurements were performed at two locations in the system: (1) oxygen storage tank pressure, and (2) ambient pressure water storage level. Three characteristics of the breadboard test system resulted in the oxygen tank pressure being representative of the leak rates. First, there was sufficient excess water capacity to make up for the losses while still completing the timed recharge. Second, the hydrogen storage system was proportionally smaller (1.87:1) than the oxygen storage system relative to the stoichiometry of hydrogen and oxygen in water (2:1). Third, the control algorithm allowed more than enough time for the recharge to be completed, even when the recharge time had to increase slightly to make up for the leaks. Therefore, the hydrogen tank always recovered to its target pressure, drawing on additional water as needed. The oxygen tank always fell a little short of the target pressure. The slope of this drift represented the mass losses in the system. Similarly, the water tank level drifted down as the electrolyzer drew on the excess water storage with each cycle to complete the recharge cycle.

Results are shown in Figure 9. The leak rate of hydrogen dissolved in the electro-osmotic drag water is predictable and very low at the operating pressure of this breadboard. The leak rate of the commercial scroll compressors used for hydrogen and oxygen recirculation, however, were very high and unpredictable from one cycle to the next. As a result, the leak rate estimates from one set of tests to the next varied greatly. Nevertheless, there was always a downward slope to the oxygen storage pressure and the water storage level.

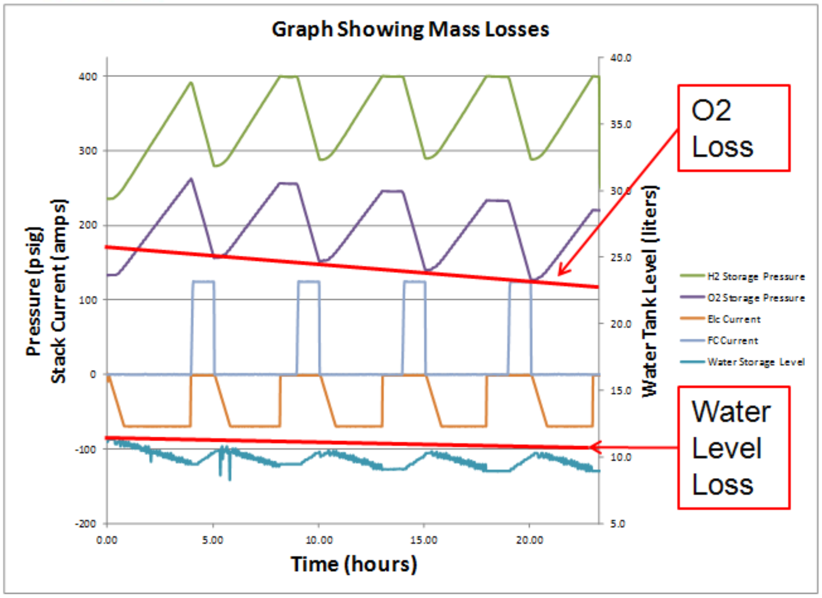

Figure 9. Baseline mass loss measurements due to COTS compressor seals and lack of hydrogen recovery

A summary of the first round of testing is shown in Figure 10 below. The initial testing was conducted with fuel cell power output of 2.2 kilowatts. Some exploratory excursions to 4.4 kilowatts were used to identify where the system limitations might be.

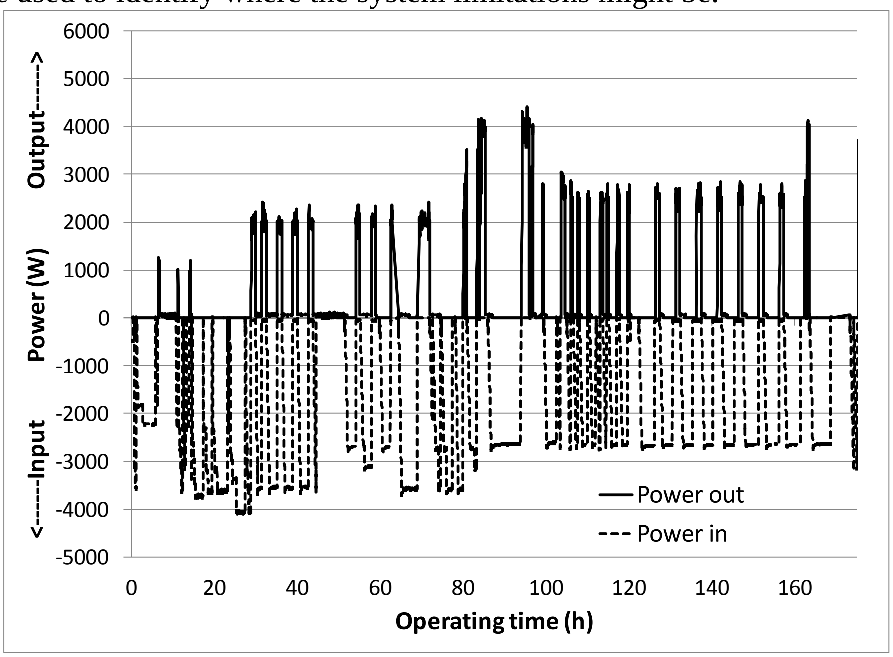

Figure 10. Summary of first round of testing

It was finally determined that the thermal system, in its original configuration, would limit us to about 2.8 kilowatts fuel cell output. Another discovery during this stage was that the electrolysis stack, which had been sitting stagnant and un-maintained for over three years, had a bad cell. As a result, from about hour 80 through 300, the electrolysis stack current was limited to 70-80% of the desired operating point. This limitation extended recharge times, but otherwise did not limit system testing. The electrolysis stack was replaced with a new, high efficiency stack at hour 300.

Minor modifications to the system were conducted between the first and second rounds of testing. First, the fuel cell cooling circuit was updated to improve cooling performance and enable operation with power output above 2.8 kilowatts. The original cooling scheme utilized direct mixing of the cold and hot fluid streams. In so doing, each time the cooling valve cycled, it would cause a pressure spike on the fuel cell coolant loop that would put the system out of manufacturer's tolerances on pressure differences across the cell plates. Furthermore, the direct mixing scheme was relatively inefficient. By inserting an additional heat exchanger and reworking the piping, the fuel cell temperature control could be maintained in a stable way up to the 4 kW rating of the fuel cell stack.

A second modification involved improvement of the fuel cell reactant pressure regulation system, through adding a proportional flow control valve in parallel with the oxygen feed regulator in the fuel cell reactant feed circuit. As a result, the proportional valve could make up for the regulator droop as flow rates increased at the higher fuel cell power level. The need for this improvement again resulted from attempting to stay within manufacturer's specifications on fuel cell pressure differences between hydrogen, oxygen, and coolant flows. From hour 170 forward, many charge-discharge cycles were completed with the fuel cell operating at this higher output power (Figure 11).

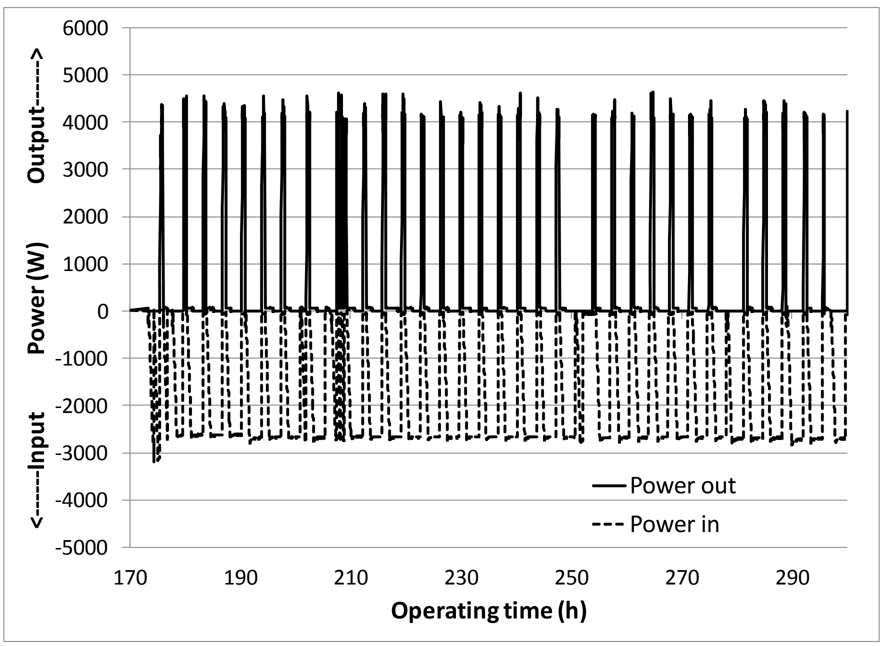

Figure 11. Demonstrated charge-discharge cycles at increased power output from 2.2 to >4 kilowatts during the second round of testing

In preparation for the final round of testing, the components being developed in Task 3 (Hydrogen Recovery Reactor) and Task 4 (Sealed Reactant Circulation) were integrated with the breadboard system. While the body of the HRR was installed in the breadboard during the initial fabrication phase, the final test incorporated the reactor media that resulted from the sub-scale testing conducted in Task 3. In addition, a new electrolysis stack was installed in the system.

This electrolysis stack included thinner membrane and advanced catalyst materials to improve the efficiency over the baseline stack, which had been installed in 2006.

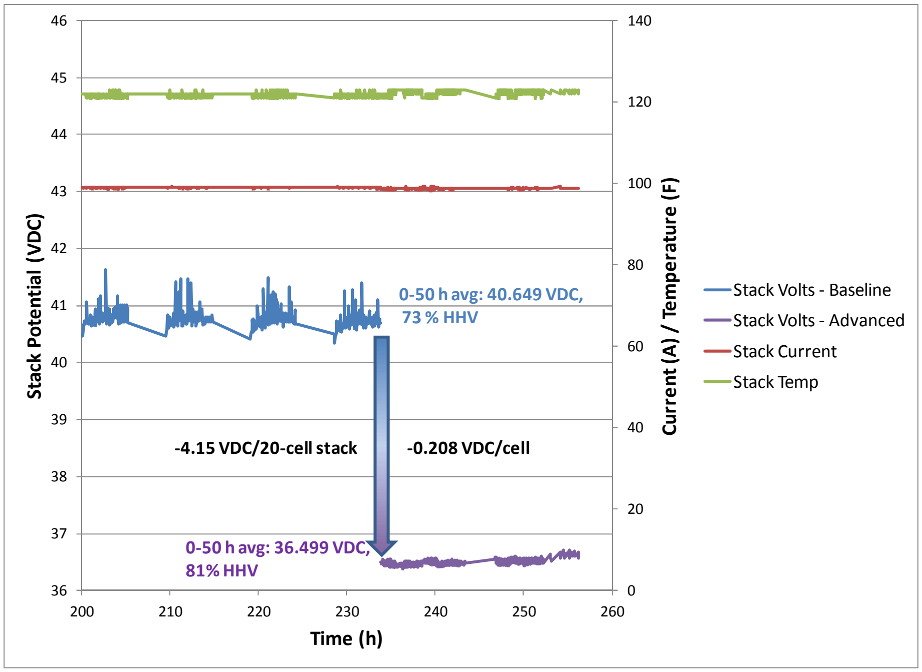

Figure 12. Improvement in electrolysis efficiency from 73% to 81% demonstrated in third round of testing

As described by Figure 12, the new electrolysis stack improved the electrolysis stack efficiency from 73% to 81% of the higher heating value (HHV) of hydrogen. This represents over 0.2 VDC decrease per cell. This summarizes some of the improvements in efficiency that Proton has implemented over the years from the original breadboard demonstration, including some of the developments funded by ONR.

During the final round of testing, the HRR was finally tested in a full-scale format. Since a sensor to measure the trace presence of hydrogen within a pressurized oxygen environment was not available, the test approach required periodic sampling of the oxygen stream to low pressure across an ambient pressure sensor. The results are shown in Figure 13 and interpreted here. The hydrogen (orange) and oxygen (purple) pressures are plotted on the right-hand vertical axis. The concentration of hydrogen in the oxygen stream is plotted on the left-hand axis in units of percent of the lower flammability limit (LFL). As the LFL is 4 percent hydrogen in oxygen, the values represented in the figure are a percentage of that 4-percent concentration. The first section of data that aligns with the two sharp drops in hydrogen pressure (0.1 h) represent the baseline sample of hydrogen concentration with the HRR system disconnected, and the hydrogen phase separator drain directed to an external low pressure tank. After the HRR system is engaged, each shallow drop in hydrogen pressure represents a drain operation from the hydrogen phase separator into the pressurized anode water circulation loop through the HRR. Each sharp drop in the oxygen pressure represents a manually engaged sample directed to the combustible gas sensor. There was no increase from the baseline hydrogen concentration after engaging the HRR. In fact, although this might be within the noise of the sensors detection limits, the general trend on hydrogen concentration was to decrease even though a water stream with dissolved hydrogen was being injected into the anode water loop. This result means that the HRR was effective at mixing those two streams and managing any hydrogen that came out of solution.

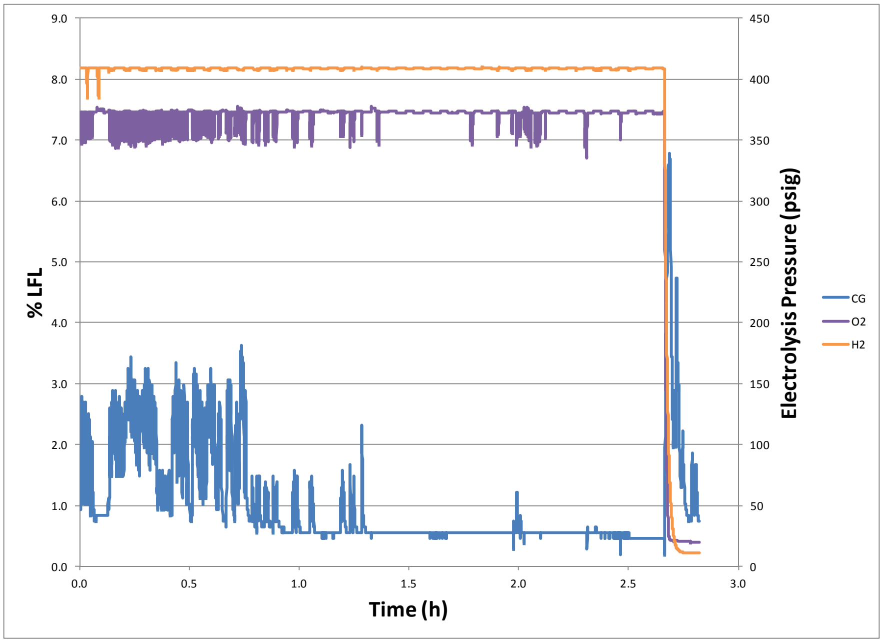

Figure 13. Results of full-scale hydrogen recovery reactor testing shows equal or lower hydrogen concentration

A summary of the test conditions during the three rounds of testing describes the progress in system capability that was demonstrated through this test program (Table 2). While the third round of testing was the shortest in duration due to the schedule limitations of the project, it represented the most complete demonstration of an air independent PEM RFC conducted with this breadboard to date (Figure 14). This successful final test incorporated all of the necessary elements that would allow a system to be demonstrated with high pressure electrolysis technology, including the hydrogen recovery reactor (Figure 15). Furthermore, the fuel cell subsystem is in a very complete state including improved pressure regulation and sealed reactant circulation compressors. Many of the components would translate directly to a more refined brassboard or representative vehicle package. The test cycles were longer, representing a deep draw-down of the tank pressures and a complete recharge. The electrolysis efficiency increased from 73% to 81%, and the power output was above 4 kilowatts.

Table 2. Test Conditions

	Round 1	**Round 2**	**Round 3**
Power output (kW)	2.2-4.0	4.0-4.4	4.0-4.4
Charge time (h)	3.5	2	6
Discharge (h)	1	0.5	2
Electrolyzer Efficiency	73%	73%	81%
Fuel Cell Efficiency	56.2%	52.2%	52.2%
Stack RTE	41.0%	38.1%	42.2%
Leakage (efficiency loss)	4.6%	5.4%	<1%

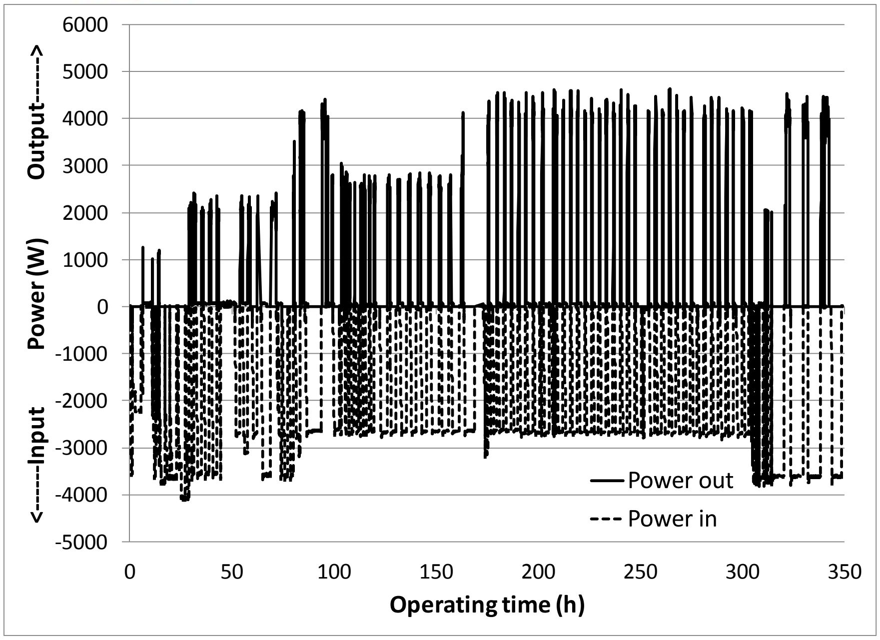

Figure 14. The stack power input and output profile from all three rounds of testing

Figure 15. Breadboard system fluids compartment at conclusion of test phase, including sealed scroll compressors and high efficiency electrolysis stack

4.0 Conclusions

As a result of the testing reported above, the state-of-the-art understanding of operating a closed-loop hydrogen-oxygen PEM regenerative fuel cell has been advanced. The system has demonstrated operation at twice the output power from previous work. The thermal management and fuel cell reactant management systems were upgraded to achieve this power increase. Furthermore, components have been built and tested that eliminate the two remaining reactant losses from the system. This testing represents a significant achievement in the development of air independent PEM RFC systems. All of the building blocks are in place to justify further development of the technology. The major risks in the fuel cell system, including fuel cell pressure regulation and especially sealed reactant circulation, have been mitigated. Within the electrolysis subsystem, the last reactant loss was mitigated by implementing the hydrogen recovery reactor and the stack efficiency was dramatically improved by implementing an advanced membrane electrode assembly. Proton has already proven electrolysis system operation at 2,400 psig in separate development efforts and a cell stack design has been completed for 5,000 psig operation. Incorporating this proven electrolysis technology with the fuel cell stack and system technology demonstrated in this test program would operate in a very similar way to the breadboard system tested here.

By incorporating proven electrolysis systems operating at 2,400 psig or 5,000 psig, the energy density of this air independent energy storage device represents a significant improvement over other state-of-the-art energy storage systems. With 5,000 psig reactant storage, the PEM system will achieve 400 Wh/L. Higher storage pressures enable even higher volumetric energy density systems.

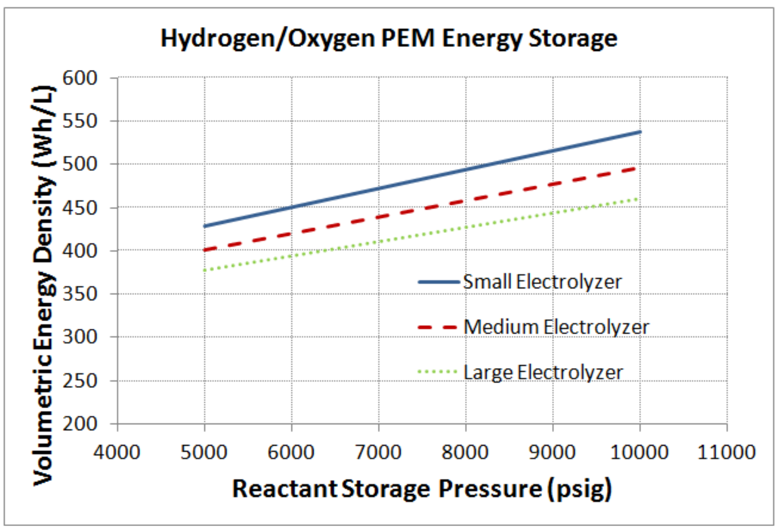

Figure 16. Energy density estimates for a PEM RFC

5.0 Recommendations

Several recommendations result from the completion of this work in order to keep the system design and development effort moving closer to fully integrated sea trials. Designing an integrated package of electrolysis and fuel cell fluid components within the required envelope for a vehicle energy section is a logical next step. Achieving an integrated package will require thorough requirements definition, comprehensive engineering, component selection and packaging. Having tested the air independent breadboard with a 400 psig electrolyzer, the team is in a strong position to incorporate proven higher pressure electrolysis hardware into the next version of the PEM RFC energy storage system. In addition to packaging the components in a relevant form factor and incorporating the higher pressure electrolysis hardware, it would also make sense to continue to utilize the existing breadboard platform to accelerate system development. For example, the breadboard can serve as a platform for system control algorithm development, further refinement and optimization of components and sub-systems that will be common to the next generation system. In addition, the breadboard may serve as a useful platform to try further integration of DC power distribution within the fuel cell components to closer mimic the way the power will be distributed in the next generation system. A conceptual model of the packaged RFC system is shown in Figure 17 below.

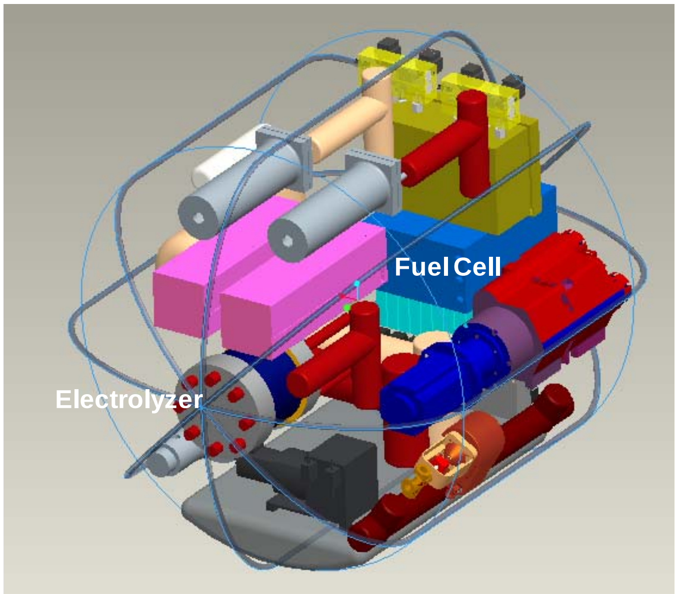

Figure 17. Preliminary package layout for an air independent PEM RFC for undersea vehicle operations

Proton recommends proceeding with more advanced system development, integrated packaging in a relevant form factor, and advanced integration of fluids, electrical, and controls hardware. A 400 Wh/L energy storage system based on an air independent, hydrogen-oxygen, PEM RFC is feasible within the near term if development efforts proceed forward.

6.0 References

1. Mitlitsky, F., A.H. Weisberg, and B. Myers, “Regenerative fuel cell systems,” *Energy & Fuels*, vol. 12, no. 1, 56-71, 12 January 1998.
2. Mitlitsky, F., B. Myers, A. H. Weisberg, T.M. Molter, and W.F. Smith, “Reversible (Unitized) PEM Fuel Cell Devices,” *Portable Fuel Cells Conference*, Lucerne, Switzerland, June 21-24, 1999.
3. Barbir, F., L.Dalton and T. Molter, “Regenerative Fuel Cells for Energy Storage: Efficiency and Weight Trade-offs,” *Proc. 1st International Energy Conversion Engineering Conference*, Portsmouth, VA, 17-21 August 2003, AIAA 2003-5937.
4. Barbir, F., L.Dalton and T. Molter, “Efficiency and weight trade-off analysis of regenerative fuel cells as energy storage for aerospace applications,” *Int. J. Hydrogen Energy*, vol. 30, pp. 351–357, 2005.
5. Barbir, F., L. Dalton and T. Molter, “Regenerative fuel cells for energy storage: efficiency and weight trade-offs,” *IEEE Aerospace and Electronic Systems Magazine*, vol. 20, pp. 35–40, March 2005.
6. Bents, D., V. Scullin, B. Chang, D. Johnson, and C. Garcia, “Hydrogen-Oxygen PEM Regenerative Fuel Cell Energy Storage System,” *Fuel Cell Seminar*, San Antonio, TX, 1-5 November 2004.
7. Garcia, C., B. Chang, D. Johnson, D. Bents, V. Scullin, and I. Jakupca, “Round Trip Energy Efficiency of NASA Glenn Regenerative Fuel Cell System,” *NHA Hydrogen Conference*, Long Beach, CA, 12-16 March 2006.
8. Hollander, S., K. Swider-Lyons, and M. Osborn, “Water-Based Propulsion for Space Applications,” *41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference*, Tucson, AZ, July 10-13, 2005, AIAA 2005-4122.
9. Dalton, L., C. Ebner, and E. Anderson, “Cycle Testing of a Closed-Loop Hydrogen-Oxygen Regenerative Fuel Cell,” *Proc. 43rd Power Sources*, Philadelphia, PA, July 7-10, 2008.
10. Baranenko, V., V. Kirov, “Solubility of Hydrogen in Water in a Broad Temperature and Pressure Range,” *Atomnaya Energiya*, vol. 66, no. 1, 24-28, January 1989 (translation Plenum Publishing Corp.).

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14. ABSTRACT

In developing technology for air independent undersea vehicle missions, a ground-test breadboard system was adapted and utilized to prove advanced components that enable closed-loop, zero emission, low signature energy storage. The system utilizes proton exchange membrane (PEM) fuel cell and electrolysis technology with proven commercial reliability, and a balance-of-plant primarily consisting of commercial-off-the-shelf (COTS) components. Initial durability testing measured the magnitude of reactant loss to the ambient atmosphere, before replacing components known to contribute to this loss as observed during tests in a previous program. Advanced components to mitigate these losses were designed and tested at a bench-top level before integrated testing within the breadboard system. A final round of cyclic testing was conducted with advanced reactant circulation during fuel cell power generation as well as complete hydrogen recovery during the electrolysis recharge period.

15. SUBJECT TERMS

Regenerative fuel cells, energy density, energy efficiency, hydrogen, oxygen, electrolysis, proton exchange membrane, PEM

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